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14. ABSTRACT

Recent successes in developing two-photon absorption (2PA) materials and applications have now created significant interest in exploring three-photon absorption (3PA) based novel optical materials and new applications. 3PA-based techniques may exhibit two major advantages: (1) much longer IR wavelengths (1.2-1.7 μm) can be used, and (2) much better beam confinement (resolution) can be achieved owing to the cubic dependence of nonlinear absorption on the local intensity of the excitation IR light. We have demonstrated efficient three-photon excitation in a number of nonlinear organic materials developed at our Institute. Applications of novel and highly efficient three-photon absorbing materials include (i) three-photon pumped (3PP) and frequency upconverted lasing, (ii) 3PA-based optical power limiting and stabilization, (iii) 3PA-based bio-imaging via IR to visible conversion, and (iv) 3PA-associated 3D data storage and microfabrication. Some recent experimental results of 3PP lasing as well as 3PA-based power limiting are briefly presented.

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New Generation Photonics Materials: Design, Development, Characterization and Applications

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Three-photon absorbing materials: characterization and applications

ABSTRACT

Recent successes in developing two-photon absorption (2PA) materials and applications have now created significant interest in exploring three-photon absorption (3PA) based novel optical materials and new applications. 3PA-based techniques may exhibit two major advantages: (1) much longer IR wavelengths (1.2-1.7 μm) can be used, and (2) much better beam confinement (resolution) can be achieved owing to the cubic dependence of nonlinear absorption on the local intensity of the excitation IR light. We have demonstrated efficient three-photon excitation in a number of nonlinear organic materials developed at our Institute or in cooperation with other research groups. The 3PA capability of a given material can be estimated by measuring the 3PA coefficient (or cross-section) at a given excitation wavelength or as a function of the excitation wavelength. The 3PA-active materials can be either highly fluorescent or non-fluorescent. Applications of novel and highly efficient three-photon absorbing materials include (i) three-photon pumped (3PP) and frequency upconverted lasing, (ii) 3PA-based optical power limiting and stabilization, (iii) 3PA-based bio-imaging via IR to visible conversion, and (iv) 3PA-associated 3D data storage and microfabrication. Some recent experimental results of 3PP lasing as well as 3PA-based power limiting are briefly presented.

1. INTRODUCTION

In recent years, multi-photon excitation related studies have generated a great deal of attention and interest in the research community. This trend is particularly enhanced by the recent progress in developing novel and highly efficient two-photon-absorption (2PA) active materials and seeking their new applications, such as two-photon absorption (2PA) based frequency-upconversion lasing,[1] optical power limiting and stabilization,[2] 3-D data storage,[3] 3-D scanning microscopy,[4] 3-D optical circuiting and microfabrication.[5]

Recent successes in reaching a substantial enhancement of two-photon absorption (2PA) in new molecular structures have now created significant interest in exploring three-photon absorption (3PA) based applications. For a 3PA process, a longer excitation wavelength in range from ~1.2 to ~1.7 μm can be used. Some of these wavelengths (such as 1.3 and 1.5 μm) are highly useful for optical telecommunications, and some other wavelengths in this range are specially suitable for biophotonic applications. The most attractive feature of 3PA process is the cubic dependence of the nonlinear absorption on the local optical intensity. This feature can provide a stronger spatial confinement so that a higher contrast and resolution in imaging can be obtained. Recently we reported the first observation of a highly directional and up-converted stimulated emission (cavityless lasing), produced by a strong simultaneous three-photon absorption at 1.3-μm in a new organic chromophore solution.[6] This achievement suggests exciting opportunities for a three-photon process in frequency-upconversion lasing, short pulse optical communications, optical power limiting and stabilization, and the newly emerging field of Biophotonics.[7]

It is well known that under the action of high intensity laser field any kind of materials may manifest nonlinear optical responses including multiphotn absorptive properties. Among them 2PA belongs to resonant third-order nonlinear optical processes, 3PA belongs to resonant fifth-order nonlinear processes, four photon absorption (4PA) belongs to resonant seventh-order nonlinear processes, and so on. According to the basic theory of nonlinear polarization of optical medium, the ratio between successive orders of the light induced electric polarization in a medium can be roughly estimated by[8]

$$\left|P^{(n)}\right| / \left|P^{(n-1)}\right| \approx |E| \cdot \left|\chi^{(n)}\right| / \left|\chi^{(n-1)}\right| \approx |E| / |E_0|. \quad (1)$$

Here, $\left|P^{(n)}\right|$ is the magnitude of the nth-order polarization in the medium, $\left|\chi^{(n)}\right|$ is the magnitude of the nth-order susceptibility that is a material parameter, $|E|$ is the magnitude of an applied monochromic optical field, and $|E_0|$ is the magnitude of the internal electric field of the atoms or molecules of which the medium is composed. For the incident light fields provided by ordinary light sources, the ratio of $|E|/|E_0|$ is usually so small that all nonlinear ($n \geq 2$) polarization responses can be neglected and no multi(≥ 2)-photon absorption can be observed. However, if the applied field is a laser radiation with moderately high spectral intensity, the ratio of $|E|/|E_0|$ can no longer be neglected. In these cases, the second-order and third-order nonlinear effects can be easily generated. Moreover, if the spectral intensity of the laser radiation can be further increased by focusing the laser beam and/or compressing the laser pulse, some higher-order (n>3) nonlinear optical effects can be expected.

Experienced researchers working in the area of nonlinear optics may find that, the 2PA effects can be easily observed in many two-photon active materials (such as dye solution, organic crystals, semiconductors, and pure organic solvents) by using pulsed laser of nanosecond duration, which could provide a local intensity ranging from 1 to 10^2 MW/cm^2. Furthermore, if the intensity levels of a focused laser beam reach to 10^3 to 10^5 MW/cm^2, the 3PA effects can be readily observed in various three-photon active media. The high peak-power pulsed laser sources (including optical parametric oscillator/amplifier) operating in the 1.2-1.7-μm wavelength range and in the 10^{-10}-10^{-13}-second duration range will be suitable for 3PA studies. In practice, the 3PA effects are much easier to be observed than previously thought according to the estimation given by Eq. (1). In fact, this estimation holds only for non-resonant nonlinear interaction, assuming that there is no real energy transfer between the applied optical fields and the medium. Multi-photon absorption belongs to resonant nonlinear interactions as there is a real energy transfer from the optical field to the medium. Because of the resonant features between the frequency combination of the incident optical fields and the eigen energy-state structures of the medium, the imaginary parts of higher-order ($n \geq 5$) susceptibilities of the medium can be drastically enhanced. For this reason it is not too difficult to conduct three-photon excitation related studies based on the currently available laser sources.

2. BASIC DESCRIPTION OF 3PA PROCESS

For simplicity here we only consider a single laser beam induced 3PA process and compare it to the 2PA process. We assume that at the frequency ν of the applied optical field, the considered medium is transparent to the incident light beam, i.e., there is no one-photon absorption at this frequency. In this case two- or three-photon absorption may occur if the following resonant conditions are fulfilled:

$$E_f - E_g = 2h\nu \ \text{(2PA)} \quad \text{or} \quad E_f - E_g = 3h\nu \ \text{(3PA)}, \quad (2)$$

where E_g is the eigen energy of the molecular ground state and E_f is the eigen energy of any of molecular excited states. The resonant nonlinear interaction between the applied intense optical field and a molecule leads to the absorption of two (or three) photons producing the excitation of the molecule from its ground state to a higher excited state. The quantum transition pictures of these two processes are schematically shown in Fig. 1, where the solid lines represent the real molecular eigen states while the dashed lines represent the virtual states which correspond to the intermediate quantum states of the whole system including both the optical field and the molecular ensemble.[8]

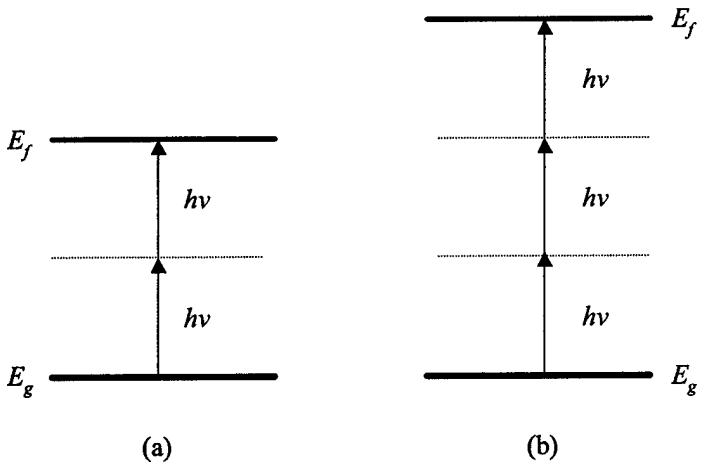

Figure 1: Quantum transition diagrams of (a) 2PA and (b) 3PA processes.

For one-beam induced 2PA and 3PA processes, the energy (frequency) for all involved photons is the same, therefore they are also called degenerate 2PA or 3PA processes. In the regime of nonlinear polarization theory, these two processes can be described by the following two nonlinear susceptibilities of the medium:

$$\left.\begin{array}{l}\chi^{(3)}(\omega,-\omega,\omega) \text{ for degenerate 2PA process} \\ \chi^{(5)}(\omega,-\omega,\omega,-\omega,\omega) \text{ for degenerate 3PA process}\end{array}\right\}. \tag{3}$$

Owing to the resonant nature of the nonlinear interaction, these two susceptibilities are complex quantities, the imaginary parts of which determine the nonlinear absorption behavior of the material.

Alternatively, the multi-photon absorption processes can also be described by the following phenomenological expression:

$$\frac{dI(z)}{dz} = -\alpha I(z) - \beta I^2(z) - \gamma I^3(z) - \eta I^4(z)\cdots. \tag{4}$$

Here $I(z)$ is the local intensity of the incident light beam propagating along z-axis, α, β, and γ are the one-, two-, and three-photon absorption coefficients of a given medium. Suppose there is no linear absorption (α=0) at the frequency (ν) of the incident light and only 2PA satisfying Eq. (2) is available, we have

$$\frac{dI}{dz} = -\beta I^2, \tag{5}$$

and its solution is

$$I(z,\nu) = \frac{I(0,\nu)}{1+\beta(\nu) z I(0,\nu)}. \tag{6}$$

Here $I(0,\nu)$ is the incident light intensity with a uniform transverse distribution, z is the propagation length in the medium, and $\beta(\nu)$ is the two-photon absorption coefficient that is a material parameter depending on the frequency of the incident light. As a macroscopic parameter, $\beta(\nu)$ (in units of cm/GW) can be further expressed as

$$\beta(\nu) = \sigma_2(\nu) N_0 = \sigma_2 N_A d_0 \times 10^{-3}, \tag{7}$$

where $\sigma_2(\nu)$ is the molecular 2PA cross-section (in units of cm^4/GW), N_0 is the molecular density (in units of $1/cm^3$), N_A is Avogadro number, d_0 is the molar concentration of the absorbing molecules (in units of M). Obviously, the cross-section $\sigma_2(\nu)$ is also a function of the light frequency for a given material.

Similarly, for a pure 3PA process, Eq. (4) becomes

$$\frac{dI}{dz} = -\gamma I^3, \tag{8}$$

leading to a solution

$$I(z,\nu) = \frac{I(0,\nu)}{\sqrt{(1+2\gamma(\nu)zI^2(0,\nu)}}. \tag{9}$$

Here, $\gamma(\nu)$ is the 3PA coefficient (in units of cm^3/GW^2) of a given material and can be further expressed as

$$\gamma(\nu) = \sigma_3(\nu)N_0 = \sigma_3 N_A d_0 \times 10^{-3}, \tag{10}$$

where $\sigma_3(\nu)$ is the molecular 3PA cross-section (in units of cm^6/GW^2). Once again, it should be noted that both $\gamma(\nu)$ and $\sigma_3(\nu)$ are the functions of frequency of the incident light. The nonlinear transmissivity of a given three-photon absorbing material of length l is defined as

$$T = \frac{I(l)}{I(0)} = \frac{1}{\sqrt{1+2\gamma l I^2(0)}}. \tag{11}$$

In practice, the value of 3PA coefficient γ can be experimentally determined by simply measuring the nonlinear transmissivity T at a known input intensity level. Once γ value is known for a given incident light frequency (or wavelength) the corresponding cross-section values of σ_3 can be further determined by using Eq. (10). On the other hand, in principle, the values of σ_2 and σ_3 can also be theoretically estimated for a given material provided that the complete information about molecular eigen state structure and transition parameters is known. Unfortunately, for most commonly studied organic materials, the specific molecular eigen-state structures and transition properties are very complicated. That makes the theoretical calculation and simulation extremely difficult.

3. THREE-PHOTON ACTIVE MATERIALS

Generally speaking, all highly two-photon active materials can also be good candidates for three-photon excitation studies. The only thing that does matter is choosing the proper range of excitation wavelength λ_{exc}. For example, if the linear (one-photon) absorption band of a given nonlinear absorbing material is located around λ_0 and in the range of wavelengths significantly longer than λ_0 there is no linear absorption, for two-photon excitation we may choose the range of

$$\lambda_0 << \lambda_{exc} \le 2\lambda_0. \quad \text{(for 2PA)} \tag{12}$$

Similarly, for three-photon excitation we may choose the range of

$$2\lambda_0 << \lambda_{exc} \le 3\lambda_0. \quad \text{(for 3PA)} \tag{13}$$

The semi-empirical condition given by Eq. (12) is based on the published experimental results of 2PA spectral measurements, which showed that the peak wavelength of 2PA band for a given sample material was located on the position either close to $2\lambda_0$ or shorter than $2\lambda_0$. For three-photon excitation the condition given by Eq. (13) is based on an extrapolated consideration since so far there is lack of results of 3PA spectral measurements.

For example, various dye solutions or dye-doped matrices are commonly used for 2PA studies. Assuming the major linear absorption band is located around (0.4~0.5) μm, the proper wavelength for two- and three-photon excitation should be roughly around (0.7~1.0) μm and (1.1-1.5) μm, respectively.

It is well known that some two-photon active materials (such as dye solutions) exhibit the fluorescence emitting property as a result of 2PA processes, whereas some other two-photon absorbing materials (such as some pure solvents) may not be fluorescent at all. The situation will be the same for three-photon absorbing materials. For the fluorescent materials after 3PA the excited molecules usually relax to a lower metastable level from which they emit fluorescence. For the non-fluorescent materials, after 3PA the exited molecules will relax to the ground state through stepwise radiationless-transition processes, and the absorbed multi-photon energy will totally be converted to thermal energy of the media. Figure 2 shows the molecular transition pathways of these two types of multi-photon absorbing materials. Obviously, the first type of materials are suitable for frequency-upconversion lasing and imaging, while the second type of materials are useful for optical power limiting, data storage and processing, and optical fabrication.

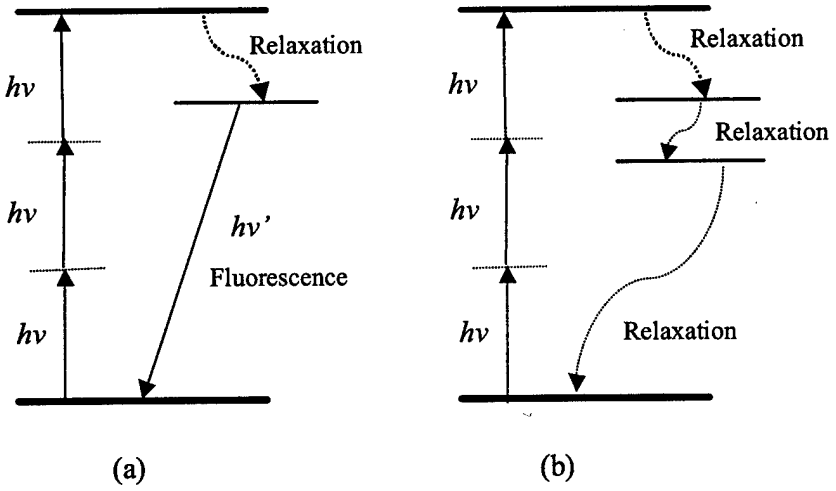

Figure 2: Molecular transition pathways of two types of three-photon absorbing materials: (a) fluorescent and (b) non-fluorescent.

4. CHARACTERIZATION OF THREE-PHOTON ABSORBING MATERIALS

(1) 3PA coefficient and cross-section measurements

For a given excitation wavelength of input laser pulses, the 3PA coefficient γ and cross-section σ_3 can be experimentally determined by simply measuring the nonlinear transmission behavior of a given sample medium. Assuming that the linear absorption is negligible at the excitation wavelength and 3PA is the major mechanism for the observed nonlinear absorption, the nonlinear transmissivity of the tested material is described by Eq. (9). In this case, once we know the value of the input intensity $I(0)$ and the value of the corresponding nonlinear transmissivity T, the γ value of the material can be directly determined. Furthermore, if the molar concentration of the absorbing molecules is known, the value of 3PA cross-section can be determined by using Eq. (10). Sometimes researchers may need to repeat these measurements at various different input intensity levels and make a curve of the measured values of γ as a function of input intensity $I(0)$. If this curve obviously deviates from a horizontal line, it means that either a 3PA saturation effect or the reverse-saturation (excited-state absorption) effects plays a certain role for the measured results under the given experimental conditions.

(2) 3PA spectral measurement

As we emphasized in Section 2, 3PA coefficient γ and cross-section σ_3 for any a given material is a function of the wavelength of the input light beam. In this sense it is not enough to evaluate different three-photon absorbing materials at a single or limited number of excitation wavelength. From the view-point of applications, we must to know what is the most efficient excitation wavelength for a given 3PA materials. For these reasons it is more desirable to measure the three-photon absorptivity as a function of wavelength (λ), i.e. the spectral distribution curve of γ or σ values versus λ.

The following are the basic requirements for 3PA spectral measurements.

(i) There should be a tunable laser or coherent light source;

(ii) The output intensity of this source should be high enough to produce a measurable nonlinear transmissivity change for a given sample medium;

(iii) The wavelength tunable range should be broad enough to cover the major part of 3PA band.

Some of tunable lasers and optical parametric generators can partially or almost fully meet these requirements. In these cases, at a constant intensity level (or known intensity levels) the nonlinear transmissivity can be measured as a function of the input light wavelength. Mostly it will be a time consuming and multi-points measurement procedure. A alternative or even better approach for 2PA and 3PA spectral measurements is the use of white-light continuum generation as a super-broad-band coherent light source to measure the nonlinear absorption spectrum of a given sample.[9,10] The distinct advantages of this technical approach are its super-broad wavelength covering range, time saving, and with no need of wavelength tunability. For example, the whole nonlinear absorption spectrum, in principle, can be measured by a single or limited number of input continuum generation pulses. Comparing the measured 2PA and 3PA spectral structures with the linear spectral structures of a given sample medium, researchers may obtain very useful insights about the differences of molecular transition pathways and selection roles for one-, two, and three-photon excitation processes, respectively.

(3) 3PA-induced fluorescence measurements

For three-photon active fluorescent materials, the 3PA-induced fluorescence measurements may provide additional scientific information about multi-photon excitation processes as well as highly useful optical parameters of the studies materials. The 3PA-induced fluorescence behaviors can be characterized by the following measurements:

(i) Fluorescence emission delay with respect to the excitation (pump) pulses;

(ii) Fluorescence emission spectral profiles;

(iii) Lifetime and temporal decay curves of fluorescence emission.

Comparing these behaviors of fluorescence emission under conditions of one-, two-, and three-photon excitation may help researchers to have a better understanding of transition pathways, selection rules, relaxation processes of the excited molecules. For this kind of measurements (particularly for item (i)), an ultrashort ($\leq$ 1ps) laser or coherent light source and a high-speed streak camera system are usually needed to provide a higher temporal resolution.[11]

For multi-photon-active fluorescent materials, their nonlinear absorption spectra could be indirectly determined by measuring the fluorescence intensity as a function of excitation wavelength if one can assume there is no linear absorption within the measured wavelength range. In this case, the actually measured is the product of nonlinear absorption coefficient and fluorescence quantum yield as a function of wavelength. One complicating factor is that the quantum yield for multi-photon excitation in a given medium doesn't have to be the same as for one-photon excitation. In this sense, researchers may not be capable to obtain concluded information of nonlinear absorption spectral curves only through the excitation spectral measurements of fluorescence emission.

5. APPLICATION OF THREE-PHOTON ACTIVE MATERIALS

(1) Advantages of using three-photon active materials

Generally speaking, all 2PA based applications can be reasonably extended to three-photon active materials. In comparison with 2PA based applications, the 3PA-based applications certainly need a higher

(more than 2-3 orders of magnitude) intensity level of the excitation sources, while they may exhibit several more attractive features as described below.

(i) A longer wavelength range (e. g. 1.2-1.7 μm) can be used for three-photon excitation, the wavelengths located in this range are more suitable either for optical telecommunication (through optical fibers), for atmosphere propagation, or for a deeper penetration of biological material (including human tissues);

(ii) A cubic relationship between the local nonlinear absorption and the local light intensity is guaranteed as shown in Eq. (8).

(iii) A narrower beam confinement and higher spatial resolution can be expected based on the merit of the cubic relationship.

To explain the third advantage of 3PA interaction, we could assume that the input focused light beam has a Gaussian transverse intensity profile near the focus point position, the transverse absorbed optical energy will have a much narrower profile than the input excitation beam due to the cubic relationship. As a result of 3PA processes, the induced fluorescence emission or induced refractive-index change will also have a much narrower transverse profile. The same consideration is also applicable to the longitudinal spatial profile; that may lead to a much better longitudinal spatial resolution for optical data storage and manufacturing. However, in some cases, the diffraction limit at longer wavelength of excitation may offset this merit.

(2) Some examples of 3PA-based applications

The following are some examples of currently available or potential applications based on three-photon absorbing materials.

(i) *Three-photon pumped (3PP) frequency-upconversion lasing*. Using 1.3-1.5-μm laser pulses of ~150 fs duration as the IR pump beam, we could generate the frequency up-converted cavityless lasing in the wavelength range of 0.5-0.6 -μm in several novel dye solutions.[6,12,13] The net conversion efficiency from the nonlinearly absorbed energy to the lasing output energy can be higher than 10%. It is particularly interesting that the backward lasing output exhibits a phase-conjugation type property based on which the thermal disturbance influence of the gain medium can be automatically concelled.[12]

(ii) *3PA-based optical power limiting and stabilization*. It has been experimentally demonstrated that the three-photon absorbing materials can be efficiently used for optical power limiting application.[14,15] In this case, the 3PA mechanism can be even better than 2PA due to the reason that under the condition of the same nonlinear transmission (e. g. T=40-70%), the output/input characteristic curves are much flatter for 3PA processes than that for 2PA processes. This feature means that a much better performance of optical power stabilization can be expected for three-photon active materials. In practice, the optical power stabilization may be very useful for optical telecommunications.[8]

(iii) *3PA-based frequency up-conversion imaging*. As we mentioned before, in comparison with 2PA mechanism, the three-photon excited imaging in fluorescent materials may posses much finer beam confinement and higher spatial resolution. Also due to the deeper penetration depth of the IR radiation of proper wavelength suitable for three-photon excitation, the interior structures or 3D-images of the sample materials that are not transparent for visible or shorter IR wavelengths can be efficiently explored.

(iv) *3PA-associate 3D-data storage and micro-manufacturing*. In these circumstances, once again, the 3PA mechanism may provide a higher data storage density in a bulk-like nonlinear medium or a better 3D-fabrication precision for optical micro-manufacturing.

6. SOME RECENT EXPERIMENTAL RESULTS

In this section, we present some preliminary results of experiments that are being conducted in our Institute in the specific directions of 3PP lasing and 3PA-based power limiting and stabilization.

(1) Novel 3PP lasing materials

A series of novel dye compounds synthesized in our Institute have been used to successfully achieve 3PP lasing in their solution phase. The chemical structures of some of them are shown in Fig. 3. .

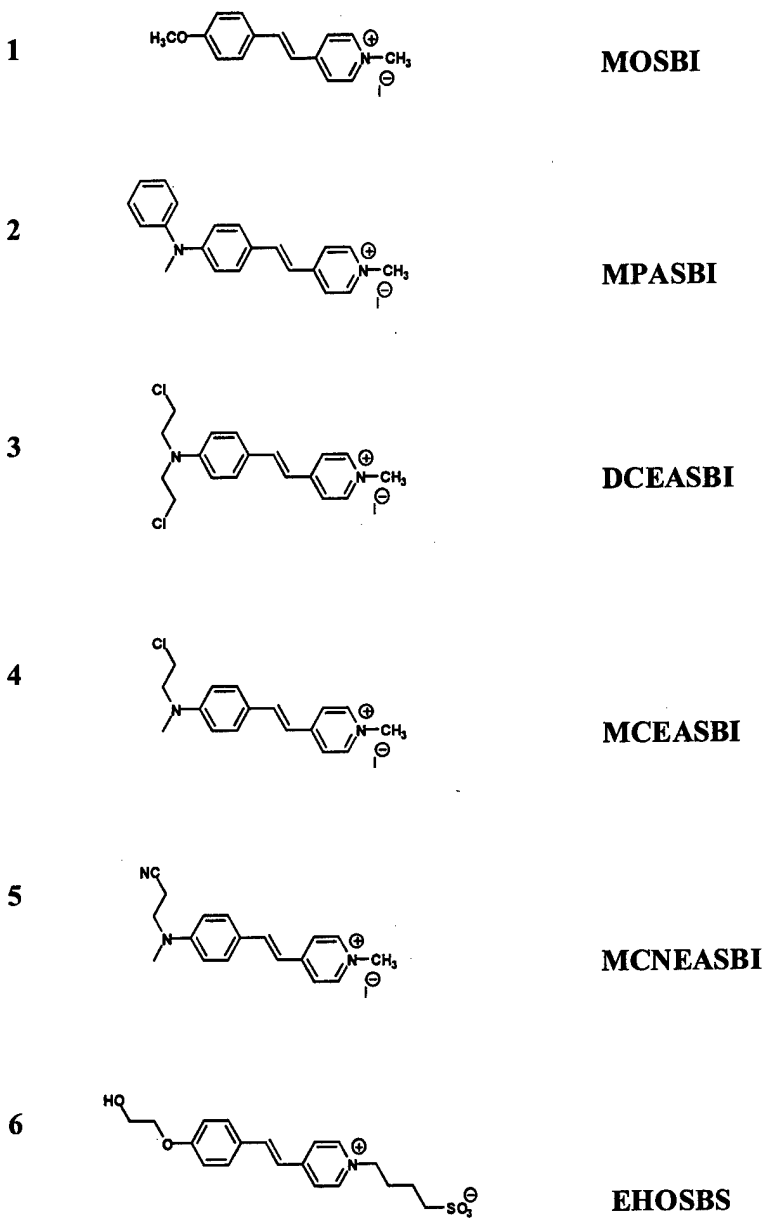

Figure 3: Chemical structures of some dye compounds generating 3PP lasing

The parameters of the pump laser beam are: wavelength ~1.33 μm, pulse duration~160 fs, beam size (before focusing) ~3 mm, divergence angle ~0.4 mrad, and pulse energy ~1-2 μJ. The IR pump beam was focused through an f=10-cm lens into the center of a 12-mm path-length glass cell filled with the tested dye solution. The key parameters of these 3PP lasing dye solutions are listed in Table 1. Among all these six dye solutions DCEASBI (#3) gives the strongest cavityless lasing output under the same experimental conditions. Two solvents, dimethyl sulfoxide (DMSO) and ethylene glycal (EG) are employed because of their good transparency at the pump wavelength and lasing wavelength.

Table 1. Key parameters of six dye solutions for 3pp lasing

Dye	Name	Solvent (molar concentration)	Lasing wavelength (nm)	Lasing bandwidth (nm)
1	MOSBI	EG (0.04 M)	~495	~ 10
2	MPASBI	DMSO (0.02 M)	~607	~13
3	DCEASBI	DMSO (0.02 M)	~579	~15
4	MCEASBI	DMSO (0.02 M)	~594	~15
5	MCNEASBI	DMSO (0.02 M)	~593	~15
6	EHOSBS	EG (0.01 M)	~496	~10

As an example, the 3PP induced fluorescence spectrum and 3PP cavityless lasing spectrum of EHOSBS (#6) solution are shown in Fig. 4. One can see that the lasing wavelength is obviously blue-shifted with a much narrower bandwidth in comparison with the fluorescence emission.

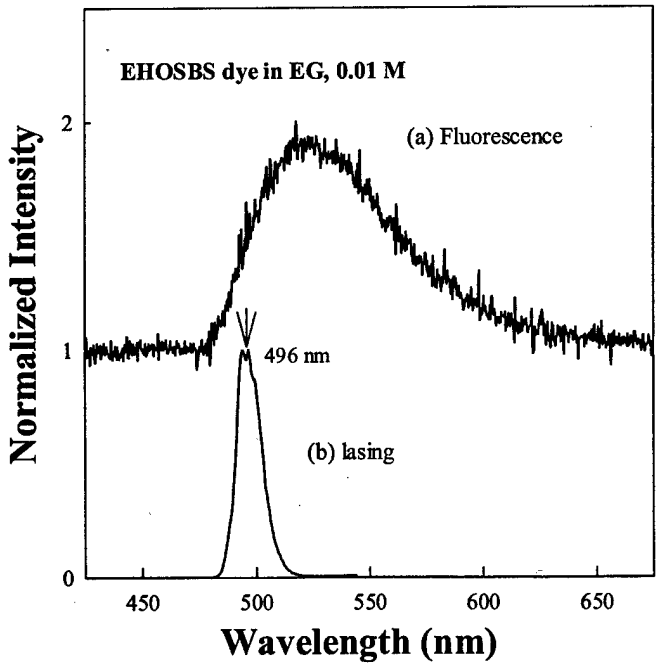

Figure 4: Measured spectral curves of (a) 3PA-induced fluorescence and (b) 3PP lasing from EHOSBS dye solution.

(2) 3PA-based power limiting measurements

We have pursued the 3PA based optical power limiting measurements in a series of chromophore solutions that have shown very strong 2PA properties. The chemical structures of two of these chromophores for applications are shown in Fig. 5.

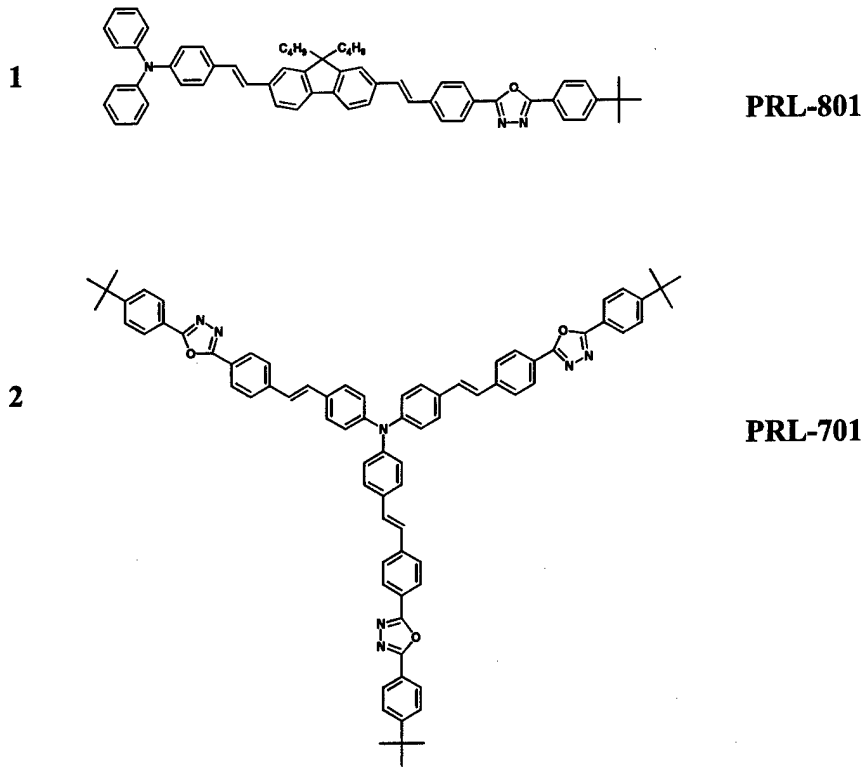

Figure 5: Chemical structures of two of three-photon absorbing chromophores for power limiting application.

The input excitation beam had basically the same parameters as used for 3PP lasing except that wavelength was 1.3 μm and input pulse energy was varied from 0.2 to 2.5-μJ in order to measure the 3PA coefficient (γ) values for sample solutions. The input IR beam was focused through an f=10-cm lens into the center of a 1-cm path-length quartz cuvette filled with the sample solution. The γ values were determined by measuring the nonlinear transmissivity as a function of the input light energy (or intensity). Table 2 gives the key measured results for these three-photon absorbing chromophore solutions in tetrahydrofuran (THF).

Table 2. Measured 3PA parameters for two chromophore solutions excited with 1.3-μm laser beam

Chromophore	Name	Solvent (concentration)	3PA coefficient γ (cm^3/GW^2)	3PA cross-section σ_3 (cm^6/GW^2)
1	PRL 801	THF (0.04 M)	0.55×10^{-5} (±15%)	2.28×10^{-25} (±15%)

As an example, Figure 6 shows the measured values of nonlinearly transmitted signal intensity as a function of input intensity for a 1-cm path-length PRL-801 solution in THF and a pure THF sample respectively. The solid-line and dash-dot-line curves are the theoretical fitting curves with the best fitting values of γ respectively. It is noted that the 3PA contribution from the solvent is less than 1/10, while the chromophore solution manifests a fairly good performance of optical power limiting.

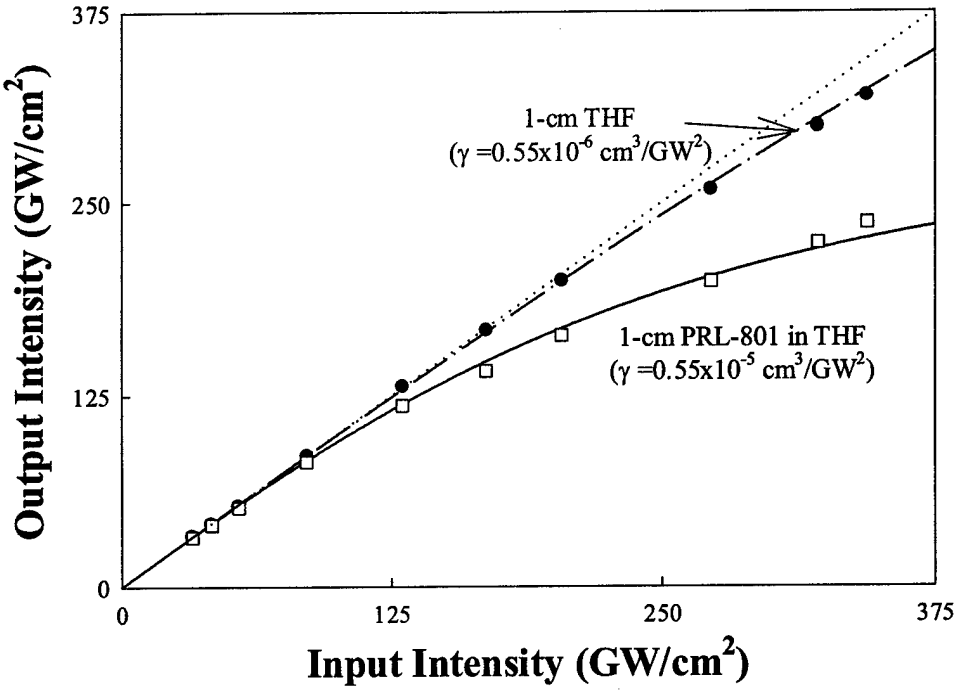

Figure 6: Output/input characteristic curves of 1-cm path-length PRL-801 solution in THF (solid line) and 1-cm path-length pure THF (dash-dot line).

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REFERENCES

1. G. S. He, J. D. BhawalkarC. F. Zhao, C.-K. Park, and P. N. Prasad, *Opt. Lett.* **20**, 2393-2395, 1995.
2. G. S. He, G. C. Xu, P. N. Prasad, B. A. Reinhardt, J. C. Bhatt, R. McKellar, and A. G. Dillard, *Opt. Lett.* **20**, 435-437, 1995.
3. D. A. Parthenopoupos and P. M. Rentzepis, *Science*, **245**, 843-845, 1989.
4. W. Denk, J. H. Strickler, and W. W. Webb, *Science*, **248**, 73-76,1990.
5. B. H. Cumpston *et al.*, *Nature*, **398**, 51-54,1999).
6. G. S. He, P. P. Markowicz, T.-C. Lin, and P. N. Prasad,. *Nature*, **415**, 767-770, 2002.
7. P. N. Prasad, *Introduction to Biophotonics*, Wiley, New York, 2003.
8. G. S. He and S. H. Liu, *Physics of Nonlinear Optics*, World Scientific, Singapore, 2000.
9. A. Negres, E. W. Van Stryland, D. J. Hagan, K. D. Belfield, K. J. Schafer, O. V. Przhonska, and B. A. Reinhardt, *Proc. SPIE – Int. Soc. Opt. Eng.* **3796**, 88, 1999.

10. G. S. He, T.-C. Lin, P. N. Prasad, R. Kannan, R. A. Vaia, and L.-S. Tan, *Optics Express*, **10**, 566-574, 2002; http://www.opticsexpress.org.
11. G. S. He, J. Swiatkiewicz, Y. Jiang, P. N. Prasad, B. A. Reinhardt, L.-S. Tan, and R. Kannan, *J. Phys. Chem. A*, **104**, 4805-4810, 2000.
12. G. S. He, J. Dai, T.-C. Lin, P. P. Markowicz, and P. N. Prasad, *Opt. Lett.* **28**, 719-721, 2003.
13. G. S. He, R. Helgeson, T.-C. Lin, Q. Zheng, F. Wudl, and P. N. Prasad, *IEEE J. Quantum Electron.* **39**, 2003(in press).
14. G. S. He, J. D. Bhawalkar, P. N. Prasad, and B. A. Reinhardt, *Opt. Lett.* **20**, 1524-1526, 1995.
15. J. D. Bhawalkar, G. S. He, and P. N. Prasad, *Opt. Commun.* **119**, 587-590, 1995.